Magnetic properties of superconducting In-Bi alloys

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The superconducting properties of In+(0.5 at.%) Bi alloys with low Ginzberg–Landau parameters are investigated by various methods. The concentration dependence of the critcal temperature, critical magnetic fields, and Ginzburg–Landau parameter and the temperature dependence of the critical fields, are determined. A transition occurs at the critical concentration $C_c = 1.55$ at.% Bi, where type-I superconductivity changes into type II. Characteristic data on the transition are obtained. The flow-change state of the alloys is also investigated. The experimental results for the flow resistances correspond to curves that can be described with the aid of a temperature-dependent critical magnetic field. Two linear parts and two parts with different curvatures are observed on the voltage-current diagram. As a consequence there exist two critical currents and two flow resistances.

INTRODUCTION

In-Bi alloys with small Bi content have a small Ginzburg-Landau (GL) parameter κ. Their investigation is of interest from the point of view that it yields information on the properties of substances with parameters lying in the range where type-II superconductivity appears. With increasing Bi content, the parameter κ increases monotonically, and there exists a critical concentration C_c such that κ reaches the value $1/\sqrt{2}$. At this concentration, the type-I superconductivity (the Meissner state) goes over into type-II superconductivity (mixed state).

This is a very unique phase transition characterized by the following properties: 1) a change takes place in the order parameter describing the superconductivity; 2) the superconductivity changes from a surface phenomenon into a volume phenomenon; 3) in place of the previously existing single critical magnetic field H_c, the penetration of the magnetic field is characterized jointly by the critical fields H_{c1} and H_{c2}[1].

In the course of our experimental studies we measured the dependence of the critical temperature T_c on the concentration C, and determined by various methods the change in the critical magnetic fields as a function of the concentration and of the temperature, and found the dependence of κ on the Bi content by using three different methods.

It was observed that the dynamic magnetic properties of the state produced in the case $C > C_c$ differ from the usual properties of substances with high κ, since the motion of the magnetic flux has definite singularities, both in the dependence of resistance to the flux on the field and temperature, and in the shape of the characteristic current-voltage curves.

As is well known, an external magnetic field H penetrates into the superconductor in the interval between H_{c1} and H_{c2}. Magnetic vortices are produced and form a network of vortex filaments covering the entire sample. The equilibrium properties of the produced Abrikosov Lattice is described by the Ginzburg-Landau-Abrikosov-Gor'kov theory (GLAG)[2-3].

The nonequilibrium states can be described by a modified classical hydrodynamic theory of vortex motion[4-7]. In the presence of an external magnetic field $H_{c1} < H_c < H_{c2}$, transport current flows also through the cores of vortices in the normal state, and this is manifest in the appearance of a finite electric field E and a finite resistivity ρ_v.

It is thus possible to determine the critical current and the resistance to the magnetic flux in the case when all the magnetic vortices are pinned by the same force.

EXPERIMENTAL PROCEDURE

The experiments were performed on In-Bi samples with Bi concentration 0–5 at.%. The alloys were prepared from a metallic In and Bi of very high purity (99.9999 and 99.999%). When the samples are prepared it is important to take into account the smallness of the critical current, so as to avoid a random disturbance produced by dissipation or by heating of the samples. This was attained, on the one hand, by using thin samples, and on the other hand by suitable heat treatment. The critical current of the heat-treated sample is probably determined principally by the pinning on the Bi atoms, as is confirmed also by the fact that the higher the Bi content the larger the critical current.

Various methods of alloy preparation were developed for the purpose of obtaining high homogeneity.

1. In the simple preparation method, the necessary amounts of In and Bi were weighed and smelted at a temperature 250–300°C in a glass cylinder. This process was carried out in either a vacuum of 10^{-6} mm Hg, or in an argon atmosphere at 1–10 mm Hg, after which the alloy was rapidly cooled and cylindrical rods of In-Bi were obtained. The alloy was then heated to several degrees above the melting temperature between previously prepared glass plates, after which thin sheets of the alloy were produced by compressing the glass plates.

A precise chemical analysis has shown, however that the samples prepared in this manner contained appreciable macroscopic inhomogeneities. The latter reached 5–25 rel.% and could be altered very little by heat treatment.

2. If the batch was vibrated at acoustic frequency during the melting, or subjected to ultrasonic mixing, then the homogeneity increased by one order of magnitude. The apparatus and method developed for this purpose reduced the inhomogeneities to 2–3 rel.%. The heat treatment employed in this case consisted of keeping the finished samples for eight-ten hours in vacuum at a temperature several degrees lower than the melting point.

From among the many prepared samples, we picked those in which the concentration corresponded, within the limits of measurement error, to the nominal value.

At the same time, investigations were performed on several samples that deviated from the nominal concentration.

The samples were U-shaped. The current contacts were made of indium, and the potential contacts were soldered with Wood's metal. The useful dimensions were length 5–8 mm, width 1–1.5 mm, and thickness 50–100 μ. The ratio of the resistivities at room temperature and at helium temperature reached 3–5.

The measurements were made in a combined glass-metal cryostat. The control apparatus constructed by us[8] could maintain the temperature within 2×10^{-3} deg/hr and measure the temperature with accuracy 1×10^{-3} deg. The temperature at a given instant of time was determined from the saturated-vapor pressure of the liquid helium and from the resistance of a germanium thermometer (Scientific Instruments, Inc. Lake Worth, Florida). The measured temperature ranged from 1.63°K to the critical value T_c at the given instant.

The measurements of the flat samples were performed in each case in such a way that the magnetic field was perpendicular to the plane of the sample.

In the earlier investigations, the magnetic field was produced by an Nb_3Sn solenoid provided with a correcting coil[9]. Subsequently, to reduce the consumption of liquid helium, a computer was used to design an Nb-Ti-Zr Helmholz coil[10]. In both cases we used a wide-range power supply[11] capable of delivering 0–100 A.

The homogeneity in the central useful part of the superconducting-magnet air gap was better than 1%.

The resistance vs. temperature curves were obtained with the aid of an x-y recorder (Cimagraphe 30/40 CZ, Cimatic Electronique, Montreuil, France), the x-input of which was the voltage from a germanium thermometer and the y-input was the sample-resistance sample.

To measure the magnetization curves we used cylindrical samples 25 mm long and 1 mm in diameter. We measured the difference signal produced in a system consisting of a measuring coil with the sample and a bucking standard coil of the same dimension. The curves were obtained using integrated electronics[12].

The critical magnetic field H_{c2} was determined also by direct measurement.

The flux measurements were made at constant temperature in such a way that the voltage-current characteristics were plotted with an x-y recorder, with the external magnetic field varied as a parameter.

CRITICAL TEMPERATURE AND STATIC MAGNETIC PROPERTIES

The experiments have shown that in the investigated concentration range the critical temperature of the sample varies from 3.398 to 4.262°K. The first value pertains to C = 0 at.% and the second to C = 5 at.% Bi.

TABLE I

Concentration range, at. %	k_1	k_2
0.0–1.5	38.2	5.8
1.5–2.5	147	31
2.5–5.0	−23.7	−13.2

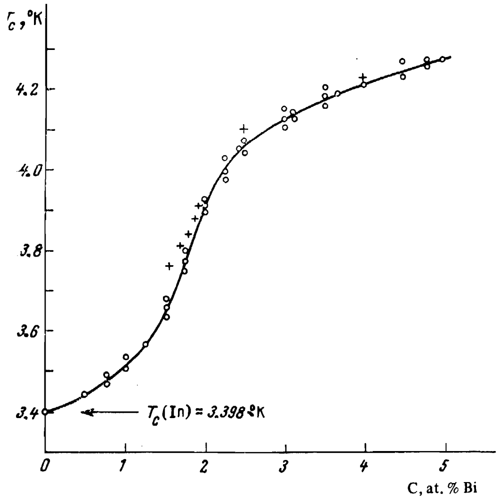

FIG. 1. T_c of In alloys with 0–5 at. % Bi vs. the Bi concentration.

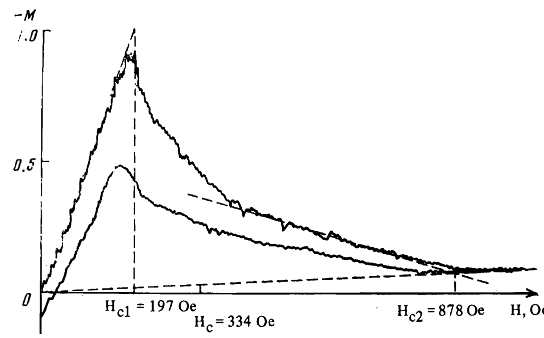

FIG. 2. M(H) plot of In + 3.0 at. % Bi alloy at T = 2.37°K.

Figure 1 shows that the dependence of the critical temperature on the Bi concentration increases monotonically. It is seen also that the $T_c(C)$ curve contains three different sections. The first (curved branch) extends to 1.5 at.% Bi, followed by a steep and almost linear region to 2.5%, and a final section with a much lower slope. By comparing the character of the curves with our earlier investigations[13, 14] we can conclude that the principal role in the formation of the central steep region is played by the change in the topology of the Fermi surface, due to contaminations.

The results of our measurements are lower everywhere than the values of T_c obtained by Kinsel et al[15, 16] (marked by crosses in Fig. 1). The reason must probably be sought in the high homogeneity of our samples.

Seraphim et al.[17] obtained an empirical formula for the dependence of T_c on the concentration:

$$\Delta T_c = T_c - T_{c0} = k_1 x + k_2 x \ln x, \tag{1}$$

where T_c is the critical point of the alloy, T_{c0} is the critical point of the pure material, $k_1 = 101.5$ at $k_2 = 17$ are constants, and x is the molar fraction. This formula, while resulting in a monotonically increasing $T_c(C)$ curve, greatly differs numerically from both our data and those of Kinsel.

Our investigations have shown that the constants mentioned above are independent of the concentration and that the analytic form of expression (1) can be used only if the average values of Table I are assumed from the different regions of the concentrations.

The plots of the magnetic moment against the magnetic field were usually obtained for individual samples at 7–12 different values of the temperature. A typical plot is shown in Fig. 2. It pertains to an alloy of In with 3.0 at.% Bi at 2.37°K.

The upper of the two curves corresponds to an increasing magnetic field, and the lower to a decreasing field. On the rising branch of the upper curve one can clearly see the initial linear section (the same as for type-I superconductors), which terminates abruptly at H_{c1}. The decreasing branch has a small curvature. H_{c2} is assumed to be equal to the point of intersection of tangents to the curve corresponding to the increasing and decreasing H (this differs from the method used by Kinsel).

The lower curve, corresponding to the decreasing field, reveals a clearly pronounced hysteresis, corresponding to a 10–15% residual magnetic flux. It is probably caused by the microscopic inhomogeneities, lattice defects, or other imperfections in the measured samples.

The thermodynamic critical magnetic field H_c was calculated from the area under the upper M(H) curve, assuming that the branches corresponding to the increasing field can be assigned a susceptibility $\chi = -1/4\pi$. All this is in good agreement with the assumptions of the GLAG theory.

The character or the type of superconductivity can be determined from the value of the parameter κ. Our measurements of the residual resistivity made it possible to estimate the value of the parameter κ of our samples, which had a short electron mean free path, from the Gor'kov-Goodman relation[3, 18]

$$\varkappa=\varkappa_0+7.5\cdot 10^3\gamma^{1/2}\rho_n. \qquad (2)$$

In the formula, κ_0 is the GL parameter of the basic material of the alloy ($\kappa_0 = 0.112$ for pure In[19]), γ is the Sommerfeld coefficient of the normal specific heat of the electrons ($\gamma_{In} = 1.61$ J/mole-deg^2 = 3.04×10^3 erg/cm^3 deg^2 [20], which varies 6.2% in the investigated concentration region), and ρ_n is the residual resistivity in Ω-cm. We present the data on the dependence of the obtained residual resistivity on the concentration:

C, at.%	1.75	2.0	3.0	4.0	5.0
$\rho_n\cdot 10^{-6}$, Ω-cm	1.59	2.21	3.24	3.57	3.72

At the same time, to determine the dependence of κ on the concentration on the basis of the $H_{ci}(T)$ or M(H) curve, the GLAG theory yields two other exact relations:

$$\sqrt{2}\varkappa=\frac{H_{c2}}{H_c}=\left(\frac{dH_{c2}}{dT}\right)_{T_c}\Big/\left(\frac{dH_c}{dT}\right)_{T_c}, \qquad (3)$$

$$4\pi\left(\frac{dM}{dH}\right)_{H_{c2},T_c}=\frac{1}{1.18(2\varkappa^2-1)} \qquad (4)$$

The three methods yielded values of κ that differed very little from one another, thus confirming the validity of the GLAG theory in the case of small parameters κ.

The obtained values are shown in Fig. 3. The κ(C) curve crosses the line $\kappa = 1/\sqrt{2}$ at a Bi content 1.55 at.%, and therefore C_c = 1.55 at.%, and is that critical concentration at which the type of superconductivity changes. Starting with this point, κ increases monotonically with concentration, and at 5 at.% it assumes a value κ = 1.68. (The crosses in the figure represent the data of Kinsel et al.[15, 16], which are close to our data at low concentrations, but differ from them by 7.5% at 2.5 and 4 at.% Bi.)

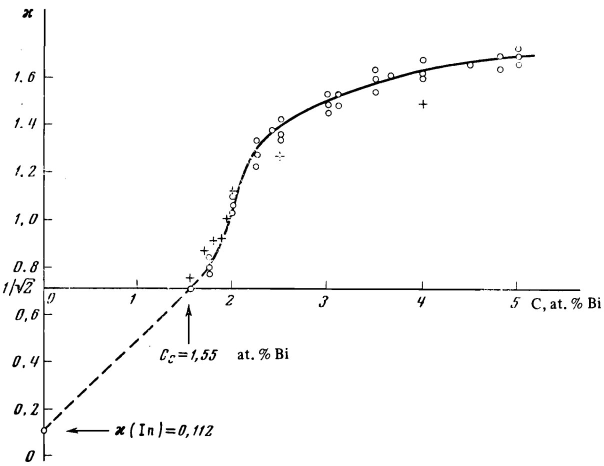

FIG. 3. Plot of κ against the Bi concentration.

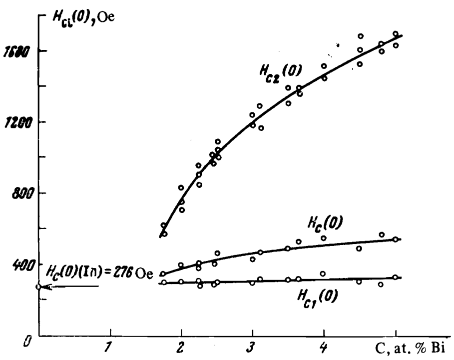

FIG. 4. Plot of $H_{ci}(0)$ against the Bi concentration.

The most important characteristic of the occurring phase transition is the critical magnetic field. Figure 4[21] demonstrates the dependence of the values of $H_{ci}(0)$ extrapolated to T = 0°K on the Bi concentration.

For In-Bi type-I superconducting alloys containing 0–1.5 at.% Bi the value of $H_c(0)$ changes by only 6.5% relative to the critical field H_c of pure In, which is equal to 276 Oe. In the vicinity of C_c = 0.55 at.%, the obtained values of the magnetic field are subject to rather large fluctuations. In the region of type-II superconductivity, 1.75–5 at.%, the value of $H_{c1}(1)$ varies from 298 to 323 Oe, $H_c(0)$ varies from 343 to 544 Oe, and $H_{c2}(0)$ varies from 585 to 1628 Oe.

Figure 5 shows the dependence of the H_{ci} curves on the temperature for two different concentrations (2.5 and 4.0 at.%). As expected, near T_c we have

$$H_{ci}(t)=H_{ci}(0)\,(1-t^2), \qquad (5)$$

where $t = T/T_c$, but H_{c2} differs noticeably from this formula, primarily at low temperatures, and when t is lower than 0.5 expression (5) no longer agrees with the experimental H_{c2}(T) curve. (This pertains to the entire investigated range of Bi content.)

Gor'kov[3] arrived with the aid of Green's functions, on the basis of the BCS theory, at the formula

$$H_{c2}(t)=\varkappa(T_c)H_c(0)\,(1.77-2.20t^2+0.50t^4-0.07t^6); \qquad (6)$$

Ginzburg[22] and Bardeen[23], using a macroscopic formalism, obtained a similar result

TABLE II

C, at.%	$H_{c2}(0)/H_c(0)$	$1.77\cdot\varkappa(T_c)$	Deviation, %	C, at.%	$H_{c2}'(0)/H_c(0)$	$1.77\cdot\varkappa(T_c)$	Deviation, %
1.75	1.71	1.42	−16.9	3.00	2.60	2.65	+1.9
2.00	2.06	1.86	−9.7	4.00	2.90	2.87	−1.0
2.50	2.41	2.44	+1.2	5.00	3,09	2.98	−3.6

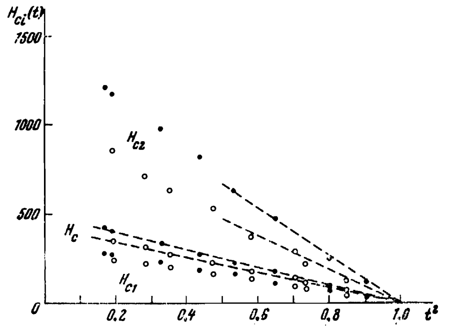

FIG. 5. Dependence of $H_{ci}(t)$ on the relative temperature of alloys containing 2.5 (○) and 4.0 (●) at. % Bi.

$$H_{c2}(t)=2\sqrt{2}\varkappa(T_c)H_c(0)\frac{1-t^2}{1+t^2}, \quad (7)$$

while Shapoval[24] derived on the basis of Gor'kov's theory the formula

$$H_{c2}(t)=3.03\varkappa(T_c)H_c(0)\alpha(t), \quad (8)$$

where $\alpha(T_c) = 0$ and $\alpha(0) = 1$.

By comparing the experimental data with these formulas at $T = 0°K$ we obtain good agreement with the result of Gor'kov, and relation (6) is valid in the entire investigated range of concentrations. By way of illustration, Table II shows, with the aid of the data of Figs. 3 and 4, the concentration dependence of the numerical values for the ratio $H_{c2}(0)/H_c(0)$ and for $1.77\kappa(T_c)$. The table shows that no systematic deviations from the Gor'kov equations are observed in our experiments. To the contrary, the deviation of the Ginzburg-Bardeen relation from the experimental values ranges from 27 to 133%, while that of the Shapoval formula ranges from 34 to 155% in the indicated concentration region.

CHANGE OF FLUX

Figures 6 and 7 show typical plots of the voltage against the current when the flux is varied in alloys containing 2.5 and 4 at.% Bi; these characteristics were

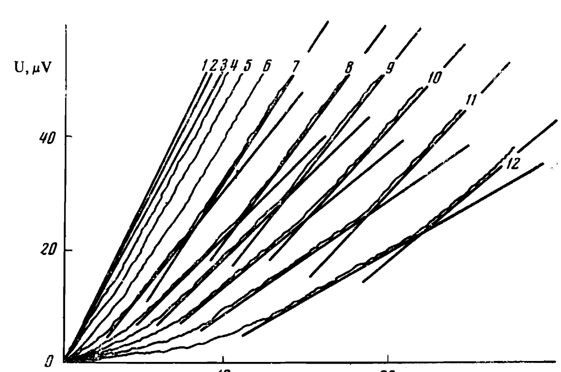

FIG. 6. Current-voltage characteristics of In + 2.5 at. % Bi sample at T = 3.098°K and at various values of H (in Oe): 1–455, 2–425, 3–400; 4–350; 5–305; 6–295; 7–285; 8–250; 9–235; 10–205; 11–185; 12–160.

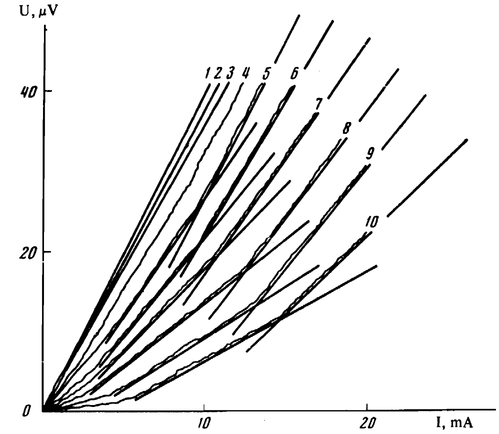

FIG. 7. Current-voltage characteristics of In + 4.80 at. % Bi sample at T = 3.763°K and at different values of H(in Oe): 1–330; 2–305; 3–280; 4–260; 5–250; 6–200; 7–180; 8–160; 9–150; 10–125.

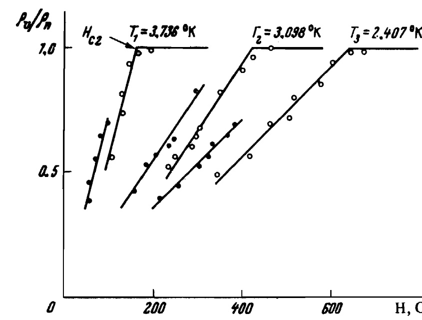

FIG. 8. Plot of ρ_v/ρ_n against H for the In + 2.5 at. % Bi alloy.

obtained with an x-y recorder by passing an increasing current through the sample. The curves were obtained with different magnetic fields.

The plots consist of three characteristic sections: so long as the vortex filaments are securely pinned no voltage appears (and there is no resistance); the succeeding curved section denotes a state of a gliding flux, and finally, in the linear region, the vortices move with constant velocity corresponding to the internal-friction coefficient. The curves show clearly (as is demonstrated also by their mathematical analysis) that each individual characteristic is characterized not by one but by two different curvatures and by two linear sections[25].

By calculating the slope for each individual value of the magnetic field and plotting it as a function of the magnetic field, we obtain the $\rho_v(H)$ characteristics, which correspond to different temperatures. Figures 8 and 9 show some of them, characterizing alloys with 2.5 and 4.0 at.%. The figures show specifically the dependence of the relative resistivities, corresponding to the same value of the voltage, on the magnetic field.

Our results for the resistance to the change of flux agree well with the formula[28]

$$\frac{\rho_v}{\rho_n}=\frac{H}{H_{c2}(T)}-K, \quad (9)$$

which describes correctly the dependence of the measured values on T and on H. This expression differs from the empirical formula of Kim et al.[27], on the one hand, in that the upper critical magnetic field contained in it depends on the temperature, and on the other, in the presence of an additional constant K. The deviation is probably connected with the fact that so long as $\kappa \sim 1$ in our experiments, they describe the motion of flux

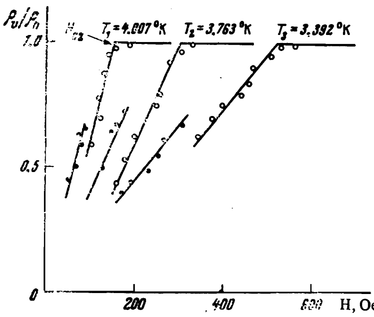

FIG. 9. Dependence of ρ_v/ρ_n on H for the In + 4.0 at.% Bi alloy.

filaments on inclusions having a Ginzburg-Landau parameter $\kappa \gg 1$.

A formula of the type (9) describes the resistance to the flux on both linear sections of the current-voltage characteristic. In the first linear region K is finite, and in the second it is equal to zero. These measurements make it also possible to determine the values of H_{c2}. The results show that the obtained values are on the average 8–10% higher than the data obtained from direct measurements of H_{c2}. The results show that the obtained values are on the average 8–10% higher than the data obtained from the direct measurements of H_{c2} or from measurements of M(H).

CONCLUSION

On the basis of our investigations we can arrive at the following important conclusions:

1. With the aid of a suitable $\kappa = \kappa(T)$, the GLAG theory describes, in agreement with the experimental observations, the characteristic properties and their change in the case of alloys with very small κ in the entire temperature region.

2. With increasing alloy concentration, at the critical value C_c, type-I superconductivity goes over into type-II superconductivity. On the basis of a precision analysis of the magnetic characteristics, in the case of any temperature-dependent κ and for any temperature, this phase transition occurs at $\kappa = 1/\sqrt{2}$.

3. Investigations of the change of the flux show that the two different curvatures on the current-voltage characteristics denote the presence of two critical currents and two resistances to the change of the flux, which can be described by a temperature-dependent critical magnetic field.

4. This indicates that one part of the magnetic vortices that are subjected to the action of the external force is set into motion while the remaining vortices are still pinned[28,29].

5. Further investigations are needed at concentrations 1 and 2 at.%. They call for very homogeneous samples with very exactly established Bi content. One can expect that they will make it possible to refine the obtained information and will yield more exact data on the character of the phase transition.

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